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SYNTHESIS, CRYSTAL STRUCTURE AND INFRARED LUMINESCENCE PRORERTIES OF Tm^{3+} DOPED OLIVINE RELATED $NaYGeO_4$ PHOSPHORS

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Abstract. Thulium containing materials attract heightened attention due to a large number of their applications in both visible and infrared (IR) spectral regions. In the IR range, Tm^{3+}-doped compounds exhibit intense emission in a broad wavelength range from 1300 nm to 2200 nm which opens the possibility of their application in medicine as well as fiber-optic communication systems. In this work, we report the synthesis, structural features and luminescence properties of Tm^{3+}-doped $NaYGeO_4$ phosphors in IR spectral region under 808 nm excitation in a wide temperature range.

The single-phase $NaY_{1-x}Tm_xGeO_4$ (x = 0.00–0.07) germanates were prepared by citrate method. The raw reagents, Y_2O_3, Tm_2O_3 and Na_2CO_3, taken in stoichiometric amounts, were dissolved in dilute nitric acid, and GeO_2 was dissolved in dilute ammonium hydroxide. Both solutions were slowly mixed, and then, citric acid was added. The obtained solution was evaporated at 150°C until a brown powder-like residue was formed. Preliminary annealing of the prepared powder was carried out by increasing the temperature stepwise from 350°C to 600°C. Then the powder was heated at 900–1050°C for 35 h with intermediate cooling and grinding.

The X-ray powder diffraction studies have confirmed that the $NaY_{1-x}Tm_xGeO_4$ (x = 0.00–0.07) germanates crystallize in the orthorhombic system (sp. gr. *Pnma*, Z = 4). The olivine structure contains layers of YO_6 octahedra located along the (100) plane which are connected to each other by chains of NaO_6 octahedra extended in the [010] direction. Isolated germanium tetrahedra are located in a sodium layers between these chains. The ionic radius of Tm^{3+} (0.88 Å for CN = 6) is smaller than that of Y^{3+} (0.90 Å for CN = 6), which leads to a monotonous decrease in the unit cell volume of $NaY_{1-x}Tm_xGeO_4$ with a gradual increase in the thulium concentration.

The diffuse reflectance spectra of germanates contain a set of bands in the visible and infrared wavelength ranges, associated with the transitions from the ground $^3H_6$ state to the excited states of Tm^{3+} ions. The broad intense bands with maxima at 790 nm and 1200 nm corresponding to the transitions to the $^3H_4$ and $^3H_5$ levels match well with the excitation wavelengths of commercial IR laser diodes. The luminescence spectra consist of two broad emission bands in 1350–1600 nm and 1600–2200 nm, which are associated with the series of cascade $^3H_4 \rightarrow {}^3F_4$ and $^3F_4 \rightarrow {}^3H_6$ transitions in Tm^{3+} ions. The maxima of the luminescence intensity of these lines are observed for different dopant concentrations: at x = 0.01 for 1400 nm line and at x = 0.07 for 1800 nm line. The process of nonradiative cross-relaxation between thulium ion pairs, $^3H_4 + {}^3H_6 \rightarrow {}^3F_4 + {}^3F_4$, becomes more efficient at high Tm^{3+} concentration, which is reflected in the luminescence spectra as growth and reduction in the intensity of the lines at 1600–2200 nm and 1350–1600 nm, respectively. The luminescence spectra of $NaY_{1-x}Tm_xGeO_4$ phosphors measured at elevated temperatures up to 200°C indicate an obvious increase in the intensity of both emission bands, which can be associated with a small change in the absorption strength at the excitation wavelength, as was observed in apatite related germanates [1].

References

1. Structural and optical characterization of Tm^{3+}-doped apatite related $NaLa_9(GeO_4)_6O_2$ phosphors / O. A. Lipina, Ya. V. Baklanova, L. L. Surat [et al.] / Ceram. Int. – 2020. – Vol. 46. – P. 26416–26424.

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